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Ultra strong polymer fibers: Ab initio calculations on polyethylene

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Abstract

The Car–Parrinello technique is used to study the electronic structure of orthorhombic polyethylene as well as the elastic modulus. The theoretical band structure and density of states are in very good agreement with experiments. The best experimentally realized elastic modulus is better than 86% of the presented theoretical value. Copyright © 1998 Elsevier Science B.V.

Keywords: Polyethylene; Carr–Parrinello; Mechanical properties; Electronic properties

1. Introduction

High performance polymer fibers form an important class of materials. The fibers are light and yet have excellent mechanical properties. For example, the elastic modulus of such fibers can exceed the modulus of steel. With special techniques the fibers are processed from ultra-high molecular weight polymers, in such a way that the long molecular chains have near crystalline orientation. An increase in the crystallinity and in the chain length improves the performance. Hence, the physical properties of the best polymer fibers will resemble the properties of the 100% crystalline polymer comprised of chains of infinite length. The study of this ideal material can provide a clue how the fibers can be improved and how much can be gained in the performance of the actual material.

The Car–Parrinello technique [1] is very useful in studying the properties of the ideal material: it allows the molecular chains to relax under forces which are calculated from the electronic structure, computed within the density functional theory. In this way, it can provide values for mechanical properties of the ideal material, like the elastic modulus, as well as information on the electronic structure.

The polymer under consideration here is polyethylene, as it is the simplest polymer and yet of technological relevance. A detailed report on the elastic modulus is reported elsewhere [2] and will be briefly summarized. The details on the electronic structure are presented here.

2. Computational details

The Car–Parrinello technique is based on the density functional theory and the local density approximation is used to describe the exchange–correlation energy. In the present study the `fhi93cp` code [3] was used. Only the valence electrons are treated explicitly; the ionic core is described by BHS-pseudopotentials

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[4] as given in [5]. The electronic wave functions are expanded in a plane wave basis set. The size of this set is controlled by a cut-off energy; in this case 54 Ry was sufficient to converge the elastic modulus. To sample the Brillouin-zone integration 12 k-points are used. More technical details can be found in [2].

The ideal material which corresponds to the high performance polyethylene fibers is the orthorhombic crystal with two monomers per unit cell. The a-axis and b-axis, perpendicular to the chain direction (c-axis), are fixed at the experimental values measured at a temperature of 4 K ($a = 7.12$ Å and $b = 4.85$ Å) [6], as no temperature effects are included. The c-axis is optimized ($c = 2.53$ Å). The orientation of the chains is such that one chain makes an angle $\phi = 42°$ with the ac-plane and the other an angle of $-\phi$. No symmetry constrains are imposed during simulation, only the form of the unit cell is kept fixed.

3. The elastic modulus

The axial elastic modulus (Y_0), also known as Young's modulus, is defined as

$$Y_0 = \frac{c_0}{A}\frac{\mathrm{d}^2E}{\mathrm{d}c^2}\bigg|_{c=c_0},$$

where A is the area of the unit cell perpendicular to the chains, c_0 the equilibrium unit cell length and E the elastic strain energy per unit cell, which is at zero temperature equivalent to the total energy.

The total energy curve is calculated by taking unit cells of different length in the c-direction and relaxing the atomic positions for each unit cell. From this energy curve the equilibrium unit cell length can be extracted as well as the second derivative of the energy at equilibrium length. The value of c_0 is found to be 2.53 Å, which is less than 1% smaller than the experimental value at 4 K ($c_0 = 2.548$ Å) [6]. Eq. (1) gives the elastic modulus $Y_0 = 334$ GPa.

To compare this value with other theoretical values, one should notice that almost all other theoretical values are calculated for a single chain and the value of A is chosen to be of room temperature ($A = 36.48$ Å^2 [7]). Using this value in Eq. (1) Young's modulus becomes 316 GPa, this procedure is validated in [2]. This is 5% larger than the value of the most recently reported ab initio calculation, $Y_0 = 300$ GPa [8]. It is about 10% smaller than calibrated semi-empirical calculations, 349 GPa [9] and 343 GPa [10].

The best performance of the actual fibers at low temperature is 288 GPa [11]. This is 86% of our presented value. As temperature effects will lower the modulus,

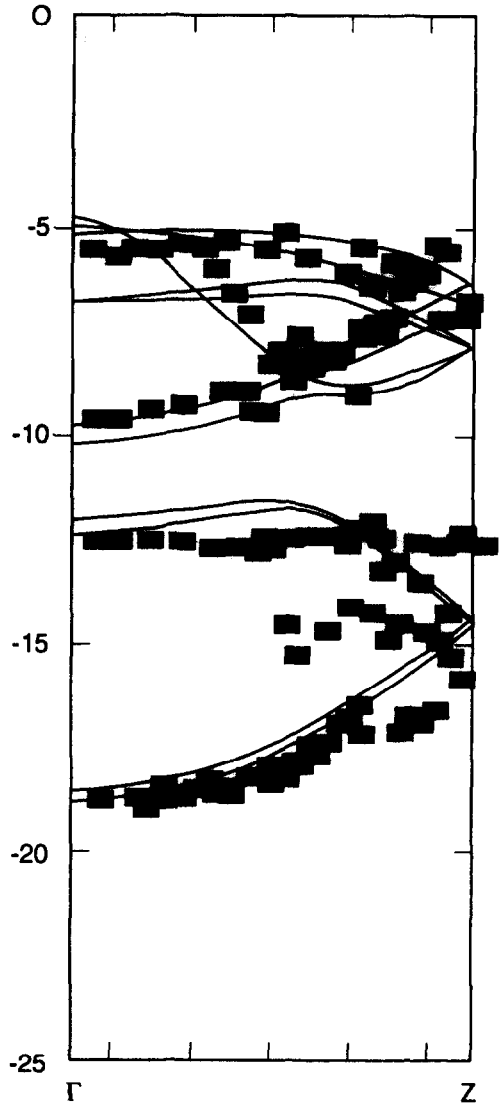

Fig. 1. The calculated valence band structure (solid lines) in the chain direction compared to the experimental band structure from ultraviolet photoelectron spectroscopy for the paraffin $C_{36}H_{74}$ (■) [12]. On the vertical axis the energy is given in eV.

it is safe to state that the best realized performance in the elastic modulus of polyethylene fibers is better than 86% of the ultimate value.

4. The electronic structure

As already mentioned, the Car–Parrinello provides next to the total energy of the relaxed system also information on the electronic structure. In Fig. 1 the bandstructure of polyethylene along the chain direction is shown as well as the angular resolved photoemission measurements by Zubrägel et al. [12] on hexatriacontane ($C_{36}H_{74}$). The zero of energy has been adjusted with 5.8 eV in order to facilitate comparison. The agreement is very good. Also, good agreement exists with the calculated bandstructure of single chain polyethylene, reported by Miao et al. [13].

The fact that this work comprises a polyethylene lattice implies that there is an influence of the interchain interaction. The interaction is most notably in the Γ–Y-direction. The occupied state of mostly H character shows a dispersion of 1.24 eV, indicating a next nearest neighbor interaction of 0.62 eV. This interaction does not necessarily indicate bonding, however. As a consequence of the interchain interaction, the direct bandgap does not occur at Γ but along the Γ–Y axis, close to Y (6.0 eV). The position of this point in k-space is determined by a subtle interplay of nearest and next nearest chain interactions.

Fig. 2 shows the density of states, convoluted with a Gaussian of FWMH (full width at half maximum) of 0.5 eV in order to facilitate with the X-ray photoelectron data of Endo et al. [14]. Very good agreement exists if one considers that the peak at 15 eV is not visible because of the small cross section of H and the

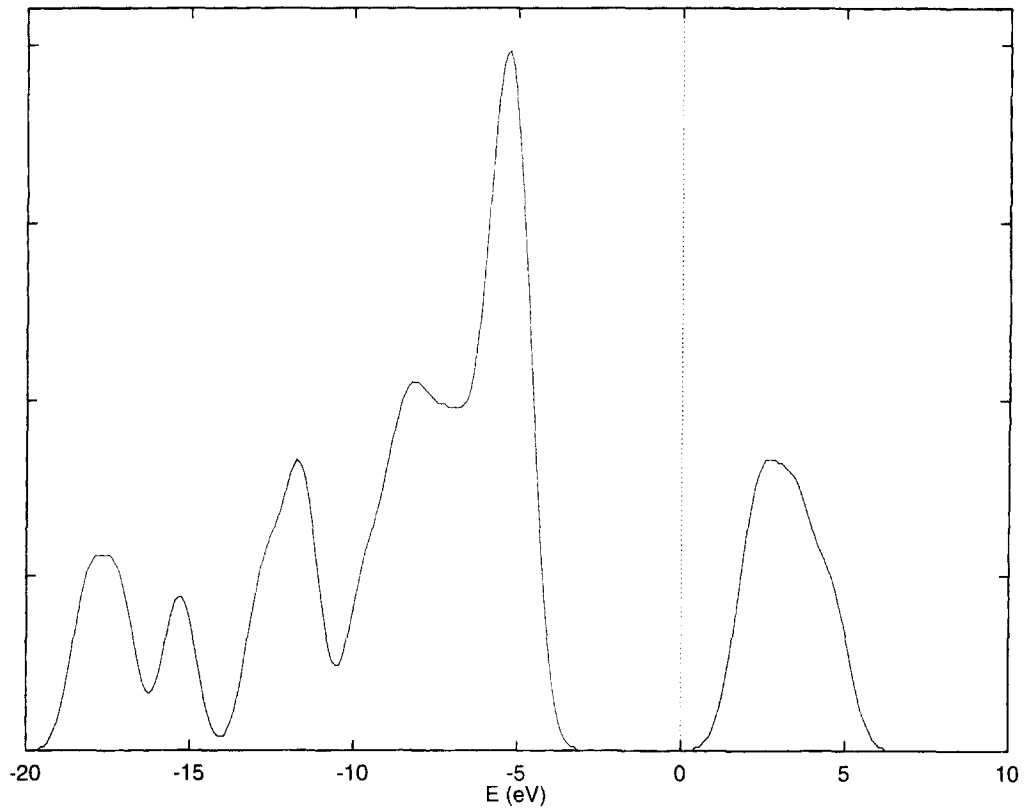

Fig. 2. The density-of-states for polyethylene, convoluted with a Gaussian of FWMH of 0.5 eV.

structure from 0 to 10 eV greatly reduces in intensity for similar reasons.

5. Conclusions

It is shown that the Car–Parrinello method is a very useful technique for polyethylene in studying the mechanical properties like the elastic modulus as well as in providing electron structure information. The properties of the crystalline polymer can be related to the experimental properties of actual materials. The bandstructure is in very good agreement with experiment. The best realized performance for the elastic modulus is really close to the ultimate performance.

References

[1] R. Car and M. Parrinello, Phys. Rev. Lett. 22 (1985) 2471.
[2] J.C.L. Hageman, R.J. Meier, M. Heinemann and R.A. de Groot, to be published.
[3] R. Stumpf and M. Scheffler, Comput. Phys. Commun. 79 (1994) 447.
[4] G.B. Bachelet, D.R. Hamann and M. Schlüter, Phys. Rev. B 26 (1982) 4199.
[5] X. Gonze, R. Stumpf and M. Scheffler, Phys. Rev. B 44 (1991) 8503.
[6] G. Avitable, R. Napolitano, B. Pirozzi, K.D. Rouse, H.W. Thomas and B.T.M. Wills, J. Polym. Sci., Polym. Lett. Ed. 13 (1973) 351.
[7] C.W. Bunn, Trans. Faraday Soc. 35 (1939) 482.
[8] B. Crist and P.G. Hereña, J. Polym. Sci. Part B 34 (1996) 449.
[9] R.J. Meier, Macromolecules 26 (1993) 4376.
[10] T. Horn, W.W. Adams, R. Pachter and P.D. Haaland, Polymer 34 (1993) 2481.
[11] P.J. Barham and A. Keller, J. Polym. Sci., Polym. Lett. Ed. 17 (1979) 591.
[12] Ch. Zubrägel, F. Schneider, M. Neumann, G. Hähner, Ch. Wöll and M. Grunze, Chem. Phys. Lett. 219 (1994) 127.
[13] M.S. Miao, P.E. van Camp, V.E. van Doren, J.J. Ladik and J.W. Mintmire, Phys. Rev. B 54 (1996) 10430.
[14] K. Endo, Y. Kaneda, M. Aida and D.P. Chong, J. Phys. Chem. Solids 56 (1995) 1131.